SYNTHESIS OF 1,3-DISILACYCLOPENTANE DERIVATIVES

N.S. Nametkin, É.D. Babich,
V.N. Karel'skii, and V.M. Vdovin

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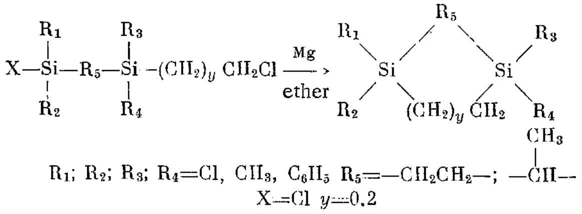
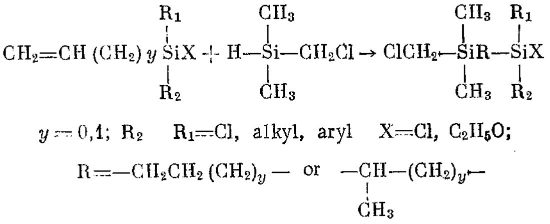
Earlier we reported on a general method for the preparation of compounds of the 1,3-disilacycloalkane series based on an intramolecular cyclization reaction of α,ω-polyfunctional organosilicon compounds containing two types of reaction centers [1]:



R_1; R_2; R_3; R_4=Cl, CH_3, C_6H_5 R_5=—CH_2CH_2—; —CH(CH_3)—
X=Cl y=0,2

(1)

The present work is concerned with the preparation of 1,3-disilacyclopentane derivatives. It is also concerned with the structure of the initial compounds used in reaction (1). We prepared them by addition of silicon hydrides containing the chloromethyl group to vinyl- and allyl chloro(ethoxy)silanes in the presence of chloroplatinic acid:



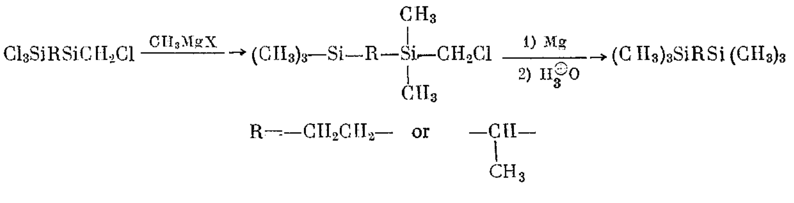
$$CH_2{=}CH(CH_2)_y\overset{R_1}{\underset{R_2}{Si}}X + H-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2Cl \rightarrow ClCH_2-\overset{CH_3}{\underset{CH_3}{Si}}R-\overset{R_1}{\underset{R_2}{Si}}X \qquad (2)$$

$y = 0,1$; R_2 R_1=Cl, alkyl, aryl X=Cl, C_2H_5O;

$R = -CH_2CH_2(CH_2)_y-$ or $-\underset{CH_3}{CH}-(CH_2)_y-$

Two isomeric products can be formed by addition of the silicon hydrides according to or against the Markovnikov rule. In the earlier work [1] we found that addition of silicon hydrides to allylsilane chlorides in reaction (2) gave 1,3-disilylpropane.

The reaction of silicon hydrides with vinylsilanes has been investigated by many authors under very different conditions [2], but the structures of the bridged compounds formed have in most cases been insufficiently investigated.* The only exception is the work described in [3] and [4]. In the latter case two structural isomers were isolated and identified. The reaction of type (2) has not been studied in relation to carbofunctional silicon hydrides. In view of the nature of the chloromethyl group we felt that it was interesting to investigate the composition of the reaction products in greater detail. For this purpose they were subjected to the changes shown in (3) to give silicanes which have been described in the literature and are therefore convenient for subsequent analysis:



$$Cl_3SiRSiCH_2Cl \xrightarrow{CH_3MgX} (CH_3)_3-Si-R-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2Cl \xrightarrow[2)\ H_3O^{\oplus}]{1)\ Mg} (CH_3)_3SiRSi(CH_3)_3 \qquad (3)$$

$R = -CH_2CH_2-$ or $-\underset{CH_3}{CH}-$

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* For this purpose infrared spectroscopy, which has comparatively low accuracy, has been used.

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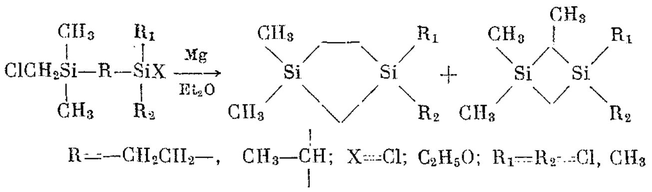
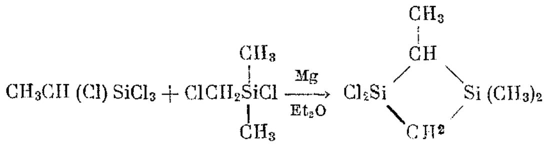
When the reaction mixture was fractionated fractions were obtained which had the same molecular weight but differed noticeably in their refractive index. The constants of the first fractions (boiling point, n_D^{20}) were found to be close to those of 1,2-bis(trimethylsilyl)ethane [4]. It is perfectly clear that the increase in melting point and refractive index in subsequent fractions (see "Experimental Method" section), in view of the known constants of the isomeric 1,1-bis(trimethylsilyl)ethane [4], can be regarded as resulting from enrichment with the latter.*

Since isolation of the individual components of the isomer mixture obtained in reaction (2) is a complicated process, we subjected the mixture to cyclization after the usual vacuum distillation. It should be expected here that two types of compound with completely different reactivity would be formed, namely the derivatives of 1,3-disilacyclopentane and 1,3-disilacyclobutane:



(4)

The silicofunctional heterocycles obtained were methylated. It was not possible to separate the methylation products and chloro derivatives of the silacycloalkanes by repeated vacuum distillation. To determine the composition of the products we carried out an alternative synthesis of one of the possible isomers, which represents a previously unknown type of four-membered silicon – carbon ring:



(5)

The dichlorodisilacyclobutane obtained was also methylated.

Chromatographic investigation of the reaction products using a synthesized standard made it possible to determine the conditions for their separation and to establish the presence in the reaction mixture of two structural isomers, namely derivatives of 1,3-disilacyclopentane and 1,3-disilacyclobutane. A characteristic property of strained four-membered silicon — carbon rings is their capacity for thermally initiated and catalytic polymerization due to opening of the ring at the endocyclic Si — C bond [5]. Having confirmed with a model of the compound that this characteristic is retained with the new type of disilacyclobutane compound, we used it to obtain the second structural isomer in pure form. For this purpose the reaction product was fractionated on a column at a fairly high temperature (200°C). It was found that it was possible to obtain the pure 1,1-dichloro-3,3-dimethyl-1,3-disilacyclopentane after only two operations. A polymer remained in the distillation vessel.†

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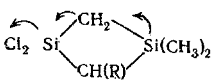
* Checking the individual fractions against Beilstein gave negative results.

† The increased tendency towards polymerization in compounds of the type:



is evidently due to increased polarity in the endocyclic Si — C bonds [5,6] adjacent to the dimethylsilyl group, and this is caused by redistribution of electron density within the ring owing to the negative inductive effect of the dichlorosilyl group. Polymerization probably occurs through the rupture of these bonds.

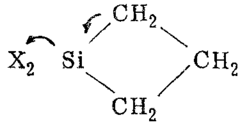
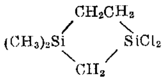
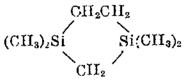
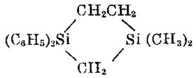
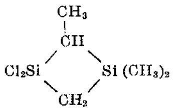
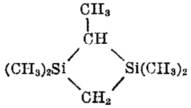
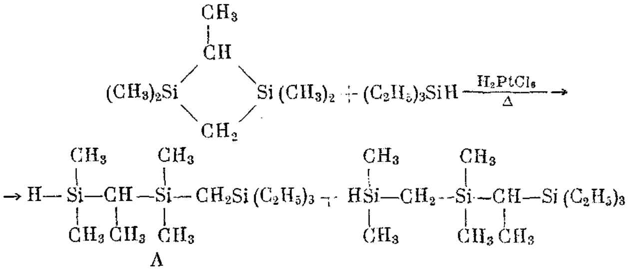
The opposite effect is observed in the case of 1-silacyclobutane derivatives of the  type:
The tendency towards polymerization decreases as a result of decreased polarity in the endocyclic Si — C bonds owing to displacement of electron density towards the heteroatom [6,7].

TABLE 1

Formula	Bp, °C (p, mm)	Yield, %	d_4^{20}	n_{20}^D	Found		Theoretical		Found, %				Theoretical, %			
					mol. wt.	*MR*	mol. wt.	*MR*	C	Si	H	Cl	C	Si	H	Cl
	176—176,7 (760)	63	1,08929	1,4747	196 191	51,48	199,32	50,93				35,70 35,60				35,5
	145—146 (760)	80,5	0,812	1,4440	151 156	51,79	158,33	51,67	53,07 53,00	35,70 35,37	11,59 11,45		53,15	35,4	11,45	
	155—156 (1,5—2)	53	1,020	1,5665	281 275	90,87	282,53	91,31	71,80 71,89	19,66	7,82 7,97		72,35	19,85	7,8	
	55—58 (9)	22	1,062	1,4690	193,2 196	52,27	199,32	50,93				35,80 35,95				35,5
	144—145 (760)	80	0,8027	1,4436	156,5 158	52,35	158,33	51,67	53,54 53,45	34,77 —	11,54 11,42		53,15	35,4	11,45	

The 1,3-disilacyclopentane derivatives can also be freed from impurities of the four-membered isomer by other methods. These include for example the telomerization reaction, which is very well known for tetramethyldisilacyclobutane* [8]:



(6)

and addition of bromine [9,10]. It was found in control experiments that changes involving opening of the hetero ring are not characteristic of pure tetramethyldisilacyclopentane. It should also be noted that these polymerization and addition reactions with opening of the ring at the same time provide independent evidence for the formation of isomeric products in the hydrosilication reaction (2) considered above. According to all the data the amount of 1,1-disilylethane structure reaches 20% with vinyltrichlorosilane; it is less (up to 10%) with vinyldimethylethoxysilane. The physicochemical characteristics of the compounds prepared are shown in Table 1.

EXPERIMENTAL METHOD

The vinylchloro(ethoxy)silanes used in the work had physical properties corresponding to those published in the literature [2]. The chloromethyldimethylsilane was prepared by the method described in [1]. The addition of silicon hydrides containing the chloromethyl group to vinylchloro(ethoxy)silanes was performed by the method described earlier [1].

Determination of Order of Addition of Chloromethyldimethylsilane to Vinyltrichlorosilane (Experiment 1). A 96-g sample of ethereal solution of the addition product from chloromethyldimethylsilane and vinyltrichlorosilane [bp 113-115°C (18 mm); $n_D^{20} = 1.4760$; composition found: 39.90, 39.85% Cl, mol. wt. 266, 263; theoretical composition: 39.5% Cl, mol. wt. 270] was treated with an ethereal solution of methylmagnesium bromide obtained from 50 g magnesium. The reaction mixture was boiled with stirring for 6 h. It was then treated with water, and the ethereal layer was removed and dried. After removal of the solvent and distillation under vacuum, 47 g methylation product was obtained. A 27-g sample of an ethereal solution of the compound was added to 3.1 g magnesium and boiled with stirring until completely dissolved. The reaction mixture was treated with water, and the ethereal layer was removed and dried. After removal of the solvent and distillation on a fractionating column with glass packing (40 cm high), 10 fractions (10 g in all) of the product were obtained (Table 2).

According to published data, the disilylethan derivatives have the following properties: $(CH_3)_3Si-CH_2\cdot CH_2-Si(CH_3)_3$, bp 151-152°C, $n_D^{20} = 1.4200$; $(CH_3)_3-CH(CH_3)-Si(CH_3)_3$, bp 160-161°C, $n_D^{20} = 1.4331$. $n_D^{20} = 1.4331$.

Synthesis of 1,1-Dichloro-3,3-Dimethyl-1,3-Disilacyclopentane (Experiment 2). The reaction was performed by the method described in [1]. From 204 g addition product from chloromethyldimethylsilane

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* In the case under consideration (reaction (6)) two types of product can form. Structure A seems preferable to us.

TABLE 2

Fraction No.	Bp, °C	n_D^{20}	Fraction No.	Bp, °C	n_D^{20}
1	152	1,4205	7	153	1,4218
2	152	1,4205	8	153	1,4218
3	151,5	1,4208	9	155	1,4218
4	152	1,4210	10	155,5	1,4220
5	152	1,4215	Residue		1,4257
6	152	1,4218	"		

and vinyltrichlorosilane and 50 g magnesium fillings, 9.5 g cyclization product was obtained. It had the following characteristics: bp 64-65°C (10 mm), $n_D^{20} = 1.4750$. Its composition was: 35.70, 35.60% Cl; mol. wt. 196, 191; $C_5H_{12}SiCl_2$. The theoretical composition is: 35.50% Cl; mol. wt. 199.32 (in benzene).

Formation of a polymer was observed when the product was distilled on a fractionating column with glass packing (50 cm high) at a temperature of 200°C. It was dissolved in benzene and methylated with an excess of methylmagnesium bromide. After removal of the solvent and vacuum distillation its molecular weight (determined cryoscopically in benzene) was 1600. The properties of the purified 1, 1-dichloro-3, 3-dimethyl-1, 3-disilacyclopentane are given in Table 1.

Preparation of 1, 1, 3, 3-Tetramethyl-1, 3-Disilacyclopentane (Experiment 3). From 30 g 1, 1-dichloro-3, 3-dimethyl-1, 3-disilacyclopentane and methylmagnesium bromide, prepared from 20 g magnesium, 19 g methylation product was obtained. Its analysis by the bromine number method [10] gave a negative result.

On cyclization, 100 g addition product from chloromethyldimethylsilane and vinyldimethyl(ethoxy)-silane [bp 112-116°C (22-23 mm); $n_D^{20} = 1.4448$; composition found: 21.5, 21.7% C_2H_5O; theoretical composition: 18.9% C_2H_5O] with magnesium in aboslute ether [1] gave 20 g tetramethyldisilacyclopentane, boiling at 144-150°C with $n_D^{20} = 1.4440$; a bromine number of 9.35/9.25 was obtained.

In order to free it from the 1, 1, 2, 3, 3-pentamethyl-1, 3-disilacyclobutane impurity 6 g of the product was boiled for 6 h with Kaufman solution prepared from 46 g sodium bromide in 100 ml absolute methanol and 2.5 g bromine. After this 3 g potassium iodide was added, and the liberated iodine was titrated with 1 N $NaHSO_3$ solution. The mixture was treated with water, extracted with ether, and dried. After distillation, 4 g tetramethyldisilacyclopentane was obtained, and its properties did not differ from those obtained above.

Preparation of 1, 1-Diphenyl-3, 3-Dimethyl-1, 3-Disilacyclopentane (Experiment 4). A 15 g yield of the product was obtained from 20 g 1, 1-dichloro-3, 3-dimethyl-1, 3-disilacyclopentane, prepared in Experiment (2), and phenylmagnesium bromide, prepared from 64 g bromobenzene.

Preparation of 1, 1-Dichloro-2, 3, 3-Trimethyl-1, 3-Disilacyclobutane (Experiment 5). A 59 g yield of the product was obtained from 268 g α-chloroethyltrichlorosilane (bp 135-137°C, $n_D^{20} = 1.4562$; composition found: 53% Cl; theoretical composition: 53.1% Cl), 193 g chloromethyldimethylchlorosilane (bp 115-117°C, $n_D^{20} = 1.4357$; composition found: 25% Cl; theoretical composition: 24.8% Cl), and 65 g magnesium by the method described in [11]. Fractional distillation under vacuum gave the dichlorosilacyclobutane, the properties of which are shown in Table 1. The mixture of the latter with 1, 1-dichloro-3, 3-dimethyl-1, 3-disilacyclopentane, obtained in Experiment (2), was separated by chromatography.

The chromatography was performed on a GCHF-18 instrument with 20% PFMS as stationary phase on INZ-1 brick. The length of the column was 4.5 m, the carrier gas was helium, and the rate was 0.55 g/cm^2. The sensitivity was 4 and the temperature 160°C. The exit time was 12 min 30 sec for dichlorotrimethyldisilacyclobutane and 13 min 30 sec for dichlorodimethyldisilacyclopentane.

Preparation of 1, 1, 2, 3, 3-Pentamethyl-1, 3-Disilacyclobutane (Experiment 6). A 17 g yield of pentamethyldisilacylobutane was obtained from 27 g 1, 1-dichloro-2, 3, 3-trimethyl-1, 3-disilacyclobutane and methylmagnesium bromide, prepared from 13 g magnesium, in ether by the method used in Experiment (3). A bromine number of 101.0/101.5 was obtained. The theoretical value is 101.2.

Reaction of 1, 1, 2, 3, 3-Pentamethyl-1, 3-Disilacyclobutane with Triethylsilane (Experiment 7). A mixture of 8 g pentamethyldisilacyclobutane and 12 g triethylsilane (bp 107-108°C, $n_D^{20} = 1.4120$) was heated in the presence of catalytic quantities of H_2PtCl_6 in an evacuated sealed tube at 170°C for 50 h. Vacuum distillation gave a 9.8-g (70%) yield of the product, boiling at 123-125°C (5-6 mm) with $n_D^{20} = 1.4670$ and $d_D^{20} = 0.842$. It contained 0.23% H, with MR = 90.53. The theoretical composition is: 0.36% H, MR 91.08.

A 20% yield of the product, with the properties shown above, was obtained in a similar manner by heating the product obtained in Experiment (2) and submitted to exhaustive methylation without preliminary fractional distillation, with triethylsilane.

Thermal Polymerization of 1, 1-Dichloro-2, 3-Trimethyl-1, 3-Disilacyclobutane (Experiment 8). A 2 g sample of the product obtained in Experiment (6) was placed in a glass tube and evacuated until the evolution of gas upon thawing ceased. The tube was sealed and heated for 6 h at 140°C. A high-molecular product, soluble in absolute benzene, was obtained with a yield of about 80%.

The authors express their sincere gratitude to M. V. Pozdnyakova for carrying out the analysis by the bromine number method.

CONCLUSIONS

1. In an investigation of the addition of chloromethyldimethylsilane to vinylchloro(ethoxy)silanes it was found that two structural isomers — derivatives of 1,1- and 1,2-bis-(organochlorosilyl)ethane — were formed.

2. A method was developed for the preparation of silicofunctional 1,3-disilacyclopentanes.

3. 1,3-Disilacyclobutanes substituted at the carbon atom were prepared for the first time, and it was found that, as also for other four-membered silicon—carbon rings, they were characterized by telomerization, polymerization, and bromine addition reactions.

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